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<p>(21) International Application Number: PCT/US96/15523 (22) International Filing Date: 27 September 1996 (27.09.96) (30) Priority Data: 60/004,545 29 September 1995 (29.09.95) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): ZHEN, Yueqian [CN/US]; 9618 Friar Tuck Drive, West Chester, OH 45069 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</p>		<p>(81) Designated States: BR, CA, JP, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: STRUCTURED AQUEOUS LAUNDRY DETERGENT COMPOSITIONS COMPRISING AMINE OXIDES</p> <p>(57) Abstract</p> <p>Heavy duty liquid detergent compositions containing an anionic surfactant component and an amine oxide surfactant are disclosed. The anionic surfactant component comprises, by weight of the composition, from about 5 % to 40 % of alkyl sulfates or alkyl polyethoxylate sulfates. The compositions are structured, provide excellent cleaning of soils, excellent softening, and are capable of suspending particles of up to about 200 microns for at least about one month.</p>		

STRUCTURED AQUEOUS LAUNDRY DETERGENT COMPOSITIONS COMPRISING AMINE OXIDES

TECHNICAL FIELD

The present invention relates to stable, aqueous heavy duty liquid laundry detergent compositions comprising anionic surfactants and amine oxide surfactants in a specific ratio to provide exceptional cleaning and softening benefits. Moreover, the detergent compositions herein are structured and have strong suspension properties. The anionic surfactant component comprises alkyl sulfates and alkyl ethoxylated sulfates.

BACKGROUND OF THE INVENTION

Numerous attempts have been made in the past to formulate laundry detergent compositions which have good cleaning properties and which are capable of suspending particles. However, such liquid detergent compositions present numerous problems to the formulator, including high viscosity at pouring shear rate, insufficient ability to suspend particles, instability during storage, and undesirable appearance.

Attempts to formulate liquid laundry detergent compositions capable of suspending solids in the past have included the use of clays or polymers which act to form a shear thinning composition. While these compositions are capable of suspending particles, many have been found to have poor physical product characteristics, including phase split. Moreover, formulators were limited to a small selection of suitable detergent ingredients in relatively low concentrations.

It has now been found that aqueous, heavy duty liquid detergent compositions containing certain anionic surfactants and amine oxide surfactants provide excellent cleaning performance, softening benefits, and attractive product characteristics, i.e., are structured, phase stable, and have a rheology which allows for the suspension of particles while being easy to pour from the product container.

Without being limited by theory, it is believed that these novel compositions have an internal structure which comprises liquid crystalline surfactant particles, also known as lamellar droplets. These particles are dispersed in the aqueous phase and are capable of suspending solids. Lamellar droplets are known in the art, e.g., H. A. Barnes, "Detergents", in K. Walters (Ed), "Rheometry: Industrial Applications", J. Wiley & Sons, Letchworth 1980. The presence of such surfactant

droplets or particles in detergent compositions may be determined by optical means or by electronic microscope, such as a transmission or scanning electron microscope.

Therefore, it is an object of the invention herein to provide a structured, aqueous heavy duty liquid laundry detergent composition which provides excellent cleaning and softening benefits and a desirable rheology.

BACKGROUND ART

Amine oxide surfactants have long been known as useful additives in laundry detergent compositions. See U.S. Patent No. 5,075,501; 5,071,594.

SUMMARY OF THE INVENTION

The present invention encompasses a structured, heavy duty liquid laundry detergent compositions having a pH of from about 5 to about 9, at 10% dilution, and comprising, by weight of the composition:

- a) from about 10% to about 40% of an anionic surfactant component which comprises, by weight of the composition:
 - (i) from about 5% to about 40% of alkyl sulfate or alkyl polyethoxylate sulfates wherein the alkyl group contains from about 10 to about 22 carbon atoms and the polyethoxylate chain contains from 0 to about 15, preferably from 0 to about 5, more preferably from 0 to about 4, ethylene oxide moieties; and
 - (ii) no more than about 5% of fatty acids;
- b) from about 1% to about 10% of an amine oxide surfactant having the formula:



- R' is selected from hydrogen, methyl and -CH₂OH; R¹ is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated and contain from about 8 to about 24 carbons, x is from 0 to about 6, y and z are intergers such that x+y+z is from about 0 to about 10; q is from 0 to about 2; EO represents ethyleneoxy; PO represents propyleneoxy; and BO represents butyleneoxy;
- when x+y+z is 0, R¹ is a hydrocarbyl moiety having chainlength of from about 8 to about 18; when x+y+z is different from 0, R¹ may be somewhat longer, having a chainlength in the range C₁₂-C₂₄;
- c) no more than about 10%, by weight, of solvents or hydrotropes; and
- d) from 0% to about 10% of a suitable electrolyte or acid equivalent thereof;

provided that the weight ratio of anionic surfactant to amine oxide surfactant is from about 1.5:1 to about 5:1; and wherein said anionic and amine oxide surfactants form liquid crystalline particles.

The compositions herein have a viscosity at 20 s^{-1} shear rate of from about 100 cp to about 4,000 cp, preferably from about 100 cp to about 2,000 cp, more preferably from about 200 cp to about 1,000 cp and are stable upon storage.

All percentages and proportions herein are by weight, and all references cited are hereby incorporated by reference, unless otherwise specifically indicated.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has now been found that a stable, aqueous heavy duty liquid detergent composition is surprisingly formed when certain anionic surfactants and amine oxide surfactants are combined at a certain pH range and in relative proportions specified hereinafter.

The compositions herein are structured and have a specific rheology. The rheology can be modeled by the following formula:

$$\eta = \eta_0 + K\gamma^{(n-1)}$$

where η is the viscosity of the liquid at a given shear rate, η_0 is the viscosity at infinite shear rate, γ is the shear rate, n is the shear rate index, and K is the consistency. As used herein, the term "structured" indicates a heavy duty liquid composition having liquid crystalline surfactant particles and an infinite shear viscosity (η_0) value between 0 and about 3,000cp (centipoise), a shear index (n) value of less than about 0.6, a consistency value, K , of above about 1,000, and a viscosity (η) measured at 20^{-1} of less than about 10,000cp, preferably less than about 5,000cp. Under low stress levels, a "zero shear" viscosity is above about 100,000cp wherein "zero shear" is meant a shear rate of 0.001 s^{-1} or less. The yield value of the compositions herein, obtained by plotting viscosity versus stress, is larger than 0.2Pa. These rheology parameters can be measured with any commercially available rheometer, such as the Carrimed CSL 100 model.

The structured compositions herein are capable of suspending insoluble particles which can be in a solid, liquid, or liquid crystalline phase. By "suspending" is meant the ability to avoid settling or physical separation of particles of up to approximately 200 microns for a period of at least about 30 days.

Relation of Zero Shear Viscosity to Suspension - The capability of a detergent composition to suspend insoluble particles is dependent on the composition's zero shear viscosity. This relationship is modeled by Stoke's Law.

$$v = 2(d_s - d_f) g.r^2 / 9.\eta$$

wherein v is the sedimentation rate of the insoluble; d_s is the density of insoluble to be suspended; d_f is the density of fluid to suspend the insoluble; g is gravity; r is radius of the insoluble; η is viscosity.

According to Stoke's Law, the rate of particle sedimentation is inversely proportional to the viscosity, i.e., the higher the viscosity, the more stable the suspension will be. Thus, a high "zero shear" viscosity is preferred, i.e., for this invention a zero shear viscosity of above about 100,000cp, preferably above about 500,000cp, even more preferably above about 1,000,000cp is desired.

The rheology and the suspending ability of these compositions are believed to be caused by the formation, in the specific compositions of this invention, of a space filling network of liquid crystalline surfactant particles (also known in the art as liposomes or vesicles) having a typical size of about 0.1 to about 10 microns. Moreover, the rheological property of the compositions herein is believed to be due in part to the presence in specific amounts of certain electrolytes, including sodium sulfate and citrate. Without being limited by theory, it is believed that the presence of electrolytes acts to control the size of the liquid crystalline surfactant particles. Thus, the structured nature of the compositions herein are affected by the choice of surfactants and by the amount of electrolytes present. In preferred embodiments herein, the compositions will further comprise from 0% to about 10%, more preferably from about 2% to about 6%, even more preferably from about 3% to about 5%, of a suitable electrolyte or acid equivalent thereof. Sodium citrate is a highly preferred electrolyte for use herein.

The compositions herein contain less than about 10%, preferably less than about 7%, more preferably less than about 5%, by weight of solvents and hydrotropes. Without being limited by theory, it is believed that the presence of solvents and hydrotropes can affect the structured versus isotropic nature of the compositions; compositions containing over about 10% solvents and/or hydrotrope lose the ability to remain in a single "phase", i.e., the composition will appear to separate into two or more layers. By "solvent" is meant the commonly used solvents in the detergent industry, including alkyl monoalcohol, di-, and tri-alcohols, ethylene glycol, propylene glycol, glycerine, etc. By "hydrotrope" is meant the commonly used hydrotropes in the detergent industry, including short chain surfactants that help solubilize other surfactants. Other examples of hydrotropes include cumene, xylene, or toluene sulfonate, urea, C₈ or shorter chain alkyl carboxylates, and C₈ or shorter chain alkyl sulfate and ethoxylated sulfates.

The heavy duty liquid laundry detergent compositions herein contain an anionic surfactant component and an amine oxide surfactant as essential ingredients.

Anionic Surfactant Component - The detergent compositions herein comprise from about 10% to about 40%, preferably from about 15% to about 25%, by weight of the detergent composition, of an anionic surfactant component. The anionic surfactant component contains alkyl sulfates and/or alkyl polyethoxylate sulfates, and may contain other non-soap anionic surfactants, or mixtures thereof. The anionic surfactant components should not contain more than about 5%, preferably less than about 1%, more preferably substantially free, of fatty acids.

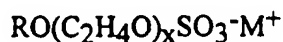
Generally speaking, anionic surfactants useful herein are disclosed in U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981, and in U.S. Patent No. 3,919,678, Laughlin et al, issued December 30, 1975, both incorporated herein by reference.

Useful anionic surfactants include the water-soluble salts, particularly the alkali metal, ammonium and alkylammonium (e.g., monoethanolammonium or triethanolammonium) salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of aryl groups.) Examples of this group of synthetic surfactants are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil.

Other anionic surfactants herein are the water-soluble salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 4 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group.

Other useful anionic surfactants herein include the water-soluble salts of esters of α -sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and β -alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Particularly preferred anionic surfactants herein are the alkyl polyethoxylate sulfates of the formula



wherein R is an alkyl chain having from about 10 to about 22 carbon atoms, saturated or unsaturated, M is a cation which makes the compound water-soluble,

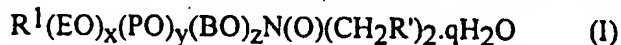
especially an alkali metal, ammonium or substituted ammonium cation, and x averages from about 1 to about 15.

Preferred alkyl sulfate surfactants are the non-ethoxylated C₁₂₋₁₅ primary and secondary alkyl sulfates. Under cold water washing conditions, i.e., less than about 65°F (18.3°C), it is preferred that there be a mixture of such ethoxylated and non-ethoxylated alkyl sulfates.

The anionic surfactant component of the present compositions comprises from about 5% to about 40%, preferably from about 7% to about 36%, most preferably from about 10% to about 25%, by weight of the detergent composition, of alkyl sulfates or alkyl polyethoxylate sulfates as described above.

Moreover, the anionic surfactant component herein must comprise no more than about 5% of fatty acids. Most preferably, the detergent compositions herein contain no fatty acids. These include saturated and/or unsaturated fatty acids obtained from natural sources or synthetically prepared. Examples of fatty acids include capric, lauric, myristic, palmitic, stearic, arachidic, and behenic acid. Other fatty acids include palmitoleic, oleic, linoleic, linolenic, and ricinoleic acid.

Amine Oxide Surfactants - The compositions herein also contain from about 1% to about 10%, preferably from about 2% to about 7%, more preferably from about 3% to about 5% by weight of an amine oxide surfactant of the formula:



In general, it can be seen that the structure (I) provides one long-chain moiety $R^1(EO)_x(PO)_y(BO)_z$ and two short chain moieties, CH_2R' . R' is preferably selected from hydrogen, methyl and $-CH_2OH$. In general R^1 is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, R^1 is a primary alkyl moiety. When $x+y+z = 0$, R^1 is a hydrocarbyl moiety having chainlength of from about 8 to about 18. When $x+y+z$ is different from 0, R^1 may be somewhat longer, having a chainlength in the range C₁₂-C₂₄. The general formula also encompasses amine oxides wherein $x+y+z = 0$, $R^1 = C_8-C_{18}$, R' is H and q is 0-2, preferably 2. These amine oxides are illustrated by C₁₂₋₁₄ alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, especially the dihydrates as disclosed in U.S. Patents 5,075,501 and 5,071,594, incorporated herein by reference.

The invention also encompasses amine oxides wherein $x+y+z$ is different from zero, specifically $x+y+z$ is from about 1 to about 10, R^1 is a primary alkyl group containing 8 to about 24 carbons, preferably from about 12 to about 16 carbon atoms; in these embodiments $y + z$ is preferably 0 and x is preferably from about 1 to about 6, more preferably from about 2 to about 4; EO represents

ethyleneoxy; PO represents propyleneoxy; and BO represents butyleneoxy. Such amine oxides can be prepared by conventional synthetic methods, e.g., by the reaction of alkylethoxysulfates with dimethylamine followed by oxidation of the ethoxylated amine with hydrogen peroxide.

Highly preferred amine oxides herein are solids at ambient temperature, more preferably they have melting-points in the range 30°C to 90°C. Amine oxides suitable for use herein are made commercially by a number of suppliers, including Akzo Chemie, Ethyl Corp., and Procter & Gamble. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers. Preferred commercially available amine oxides are the solid, dihydrate ADMOX 16 and ADMOX 18, ADMOX 12 and especially ADMOX 14 from Ethyl Corp.

Preferred embodiments include dodecyldimethylamine oxide dihydrate, hexadecyldimethylamine oxide dihydrate, octadecyldimethylamine oxide dihydrate, hexadecyltris(ethyleneoxy)dimethylamine oxide, tetradecyldimethylamine oxide dihydrate, and mixtures thereof.

Whereas in certain of the preferred embodiments R' is H, there is some latitude with respect to having R' slightly larger than H. Specifically, the invention further encompasses embodiments wherein R' is CH₂OH, such as hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2-hydroxyethyl)amine oxide.

Inventions herein comprise the detergent composition wherein the weight ratio of anionic surfactant component to amine oxide surfactant is from about 1.5:1 to about 5:1, preferably from about 1.5:1 to about 4.5:1, more preferably from about 2:1 to about 4:1, even more preferably from about 2:1 to about 3.5:1.

Optional Components - The compositions of the present invention can also preferably contain up to about 10%, preferably from 0% to about 5%, more preferably from 0% to about 3%, by weight of an ethoxylated nonionic surfactant. These materials are described in U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981, incorporated herein by reference. Preferred are the ethoxylated alcohols and ethoxylated alkyl phenols of the formula R(OC₂H₄)_nOH, wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of n is from about 5 to about 15. These surfactants are more fully described in U.S. Patent No. 4,284,532, Leikhim et al, issued August 18, 1981, incorporated herein by reference. Particularly preferred are ethoxylated alcohols having an average of from about 10 to about 15 carbon atoms in the alcohol and an average degree of

ethoxylation of from about 6 to about 12 moles of ethylene oxide per mole of alcohol.

The compositions herein also preferably contain up to about 30%, more preferably from about 1% to about 20%, most preferably from about 1% to about 10%, by weight of a non-citrate, non-fatty acid detergent builder material. While all manner of detergent builders known in the art can be used in the present compositions, the type and level of builder should be selected such that the final composition has an initial pH of from about 5 to about 9, preferably from about 6 to about 8, at a concentration of about 10% by weight in water at 20°C.

Detergent builders are described in U.S. Patent No. 4,321,165, Smith et al, issued March 23, 1982, incorporated herein by reference. Preferred builders for use in liquid detergents herein are described in U.S. Patent No. 4,284,532, Leikhim et al, issued August 18, 1981, incorporated herein by reference.

Enzymes Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, and cellulases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01% to 1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered tradename ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available

include those sold under the trade names ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985).

Amylases include, for example, α -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME (Novo) is especially useful.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Diosynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S.

Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

The enzymes employed herein may be stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species. See Severson, U.S. 4,537,706. Typical detergents, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from about 0.05% to about 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from about 0.25% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.75% to about 4%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

Other preferred components for use in liquid detergents herein are the neutralizing agents, buffering agents, phase regulants, polyacids, suds regulants, opacifiers, dispersants, such as ethoxylated tetraethylene pentaamine, antioxidants, bactericides, dyes, soil release polymers, perfumes, and brighteners described in the U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981, incorporated herein by reference. Preferred neutralizing agents for use herein are organic bases, especially triethanolamine and monoethanol amine, which results in better detergency performance than inorganic bases such as sodium and potassium hydroxides.

The compositions herein are suitable for suspending insoluble particles. Particles for suspension include alkyl amine-anionic surfactant ion pair particles, as disclosed in U.S. pat. no. 4,861,502; builders such as zeolites; bleach particles; perfume particles; encapsulated detergent additives; and other known insoluble laundry additives.

The following non-limiting examples illustrate the compositions of the present invention. All percentages, parts and ratios used herein are by weight unless otherwise specified.

EXAMPLES I-II

Liquid detergent compositions were prepared according to the following formulas.

<u>Ingredients</u>	<u>Example I</u>	<u>Examples II</u>
	% by wt.	% by wt.
C14-15AE2.25SH	--	16
C12-15AE2.5SH	16	
C45EO7	2.0	2.0
Amine oxide*	5.0	5.0
Borax	--	2.0
Citric acid	5.0	5.0

NaOH	~4	~4
H2O	balance	balance
pH	6.7	7.8
Appearance	Opaque	Opaque
	Suspension	Suspension
Zero Shear Viscosity 10 ⁶ cp	2.4	47
Viscosity (20/s) cp	750	1000

*Amine oxide is a mixture of 80% C₁₂ alkyl dimethyl amine oxide, 16% C₁₄ alkyl dimethyl amine oxide, and 4% C₁₆ alkyl dimethyl amine oxide.

The detergent samples are made by the following procedure.

The anionic surfactant paste is first mixed with alkyl ethoxylate, C₁₄₋₁₅EO7 (if present) according to the formula composition, which is followed by the addition of sodium hydroxide. Citric acid is added immediately after NaOH to bring the pH to about 5-9 at 10% solution. The amine oxide is then added. Immediately after the addition of the amine oxide, an opaque, lamellar droplet-filled suspension sample is formed. Water and other ingredients are added at the end to complete the formulation.

The compositions of Examples I and II have a viscosity/rheology capable of suspending solids and are stable for more than 30 days.

1. A structured, heavy duty liquid laundry detergent composition having a pH of from 5 to 9, at 10% dilution, and comprising, by weight of the composition:
 - a) from 10% to 40% of an anionic surfactant component which comprises, by weight of the composition:
 - (i) from 5% to 40% of alkyl sulfates or alkyl polyethoxylate sulfates wherein the alkyl group contains from 10 to 22 carbon atoms and the polyethoxylate chain contains from 0 to 15 ethylene oxide moieties; and
 - (ii) no more than 5% of fatty acid surfactants; and
 - b) from 1% to 10% of an amine oxide surfactant having the formula:

$$R^1(EO)_x(PO)_y(BO)_zN(O)(CH_2R')_2 \cdot qH_2O$$

R' is selected from hydrogen, methyl and $-CH_2OH$; R^1 is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated and contain from 8 to 24 carbons, x is from 0 to 6, y and z are intergers such that $x+y+z$ is from 0 to 10; q is from 0 to 2; EO represents ethyleneoxy; PO represents propyleneoxy; and BO represents butyleneoxy;

when $x+y+z$ is 0, R^1 is a hydrocarbyl moiety having chainlength of from 8 to 18; when $x+y+z$ is different from 0, R^1 may be somewhat longer, having a chainlength in the range C_{12} - C_{24} ;
 - c) no more than 10%, by weight, of solvents or hydrotropes; and
 - d) from 0% to 10% of a suitable electrolyte or acid equivalent thereof;

provided that the weight ratio of anionic surfactant to amine oxide surfactant is from 1.5:1 to 5:1; and wherein said anionic and amine oxide surfactants form liquid crystalline particles.
2. The composition of Claim 1 wherein said composition has a viscosity at $20s^{-1}$ shear rate of from 100 cps to 4,000 cps, preferably from 100 cps to 2,000 cps.
3. The composition of Claim 1 wherein said composition has a zero shear viscosity above 500,000cp.
4. The composition of Claim 1 wherein said composition has a pH of from 6 to 8.
5. The composition of Claim 1 comprising from 15% to 25% of the anionic surfactant component and less than 7%, by weight of solvents or hydrotropes.

6. The composition of Claim 5 wherein the anionic surfactant component of the anionic surfactant comprises from 7% to 36% alkyl ethoxylated sulfates.
7. The composition of Claim 6 wherein the anionic surfactant component comprises from 10% to 25% alkyl ethoxylated sulfates.
8. The composition of Claim 7 comprising from 3% to 5% of the amine oxide surfactant.
9. The composition of Claim 1 wherein the amine oxide surfactant is selected from the following: dodecyldimethylamine oxide dihydrate, hexadecyldimethylamine oxide dihydrate, octadecyldi-methylamine oxide dihydrate, hexadecyltris(ethyleneoxy)-dimethyl-amine oxide, tetradecyldimethylamine oxide dihydrate, and mixtures thereof.
10. The composition of Claim 9 comprising from 3% to 5% of dodecyldimethylamine oxide dihydrate, tetradecyldimethylamine oxide dihydrate, hexadecyldimethylamine oxide dihydrate, and mixtures thereof.
11. The composition of Claim 1 wherein the weight ratio of anionic surfactant component to amine oxide surfactant is from 2:1 to 3.5:1.
12. The composition of Claim 1 further comprising up to about 10% of an ethoxylated nonionic surfactant and from 1% to 20% of a non-citrate, non-fatty acid detergent builder material.
13. The composition of Claim 1 further comprising an enzyme selected from the group consisting of proteases, amylases, lipases, cellulases and mixtures thereof at a level sufficient to provide from 0.01 mg to 3 mg of active enzyme per gram of the composition.
14. The composition of Claim 1 wherein said composition is capable of suspending particles of up to approximately 200 microns for a period of at least one month.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/00 C11D1/83

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 179 054 (UNILEVER PLC.) 25 February 1987 see page 2, line 34 - line 44 see page 3, line 52 - page 5, line 24 see page 7, line 55 - line 65 see claims 1-3,5,6,11 ---	1,5-9, 11-14
A	EP,A,0 092 363 (ALBRIGHT & WILSON LTD.) 26 October 1983 see page 3 - page 4; claim 1 ---	1,5,9,12
A	US,A,4 155 871 (DONALDSON ROBERT) 22 May 1979 see claim 1; example 1 --- -/-	1,9,14

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- * "A" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US,A,5 075 501 (BORLAND JAMES E. ET AL.) 24 December 1991 cited in the application see column 4, line 53 - column 5, line 18 see claims 1-3,9-16 ---	1,9,10
A	US,A,5 071 594 (BORLAND JAMES E. ET AL.) 10 December 1991 cited in the application see claims 1-4,14-18 ---	1,9,10, 12
A	WO,A,95 05440 (THE PROCTER & GAMBLE CO.) 23 February 1995 see page 6, line 9 - page 7, line 30 see claim 1 -----	1,9,10

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